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[1] R.Pavan, P. Maia, S.Leite, S. Deflon, V. Batista. *European Journal of Medicinal Chemistry* **2010**, *45*, 1898-1905. [2] P. Yogeewari, D. Sriram, V. Veena, R.Kavya, K.Rakhra. *Biomedicine & Pharmacotherapy* **2005**, *59*, 51-55.

**Keywords:** semicarbazone, single-crystal X-ray diffraction, DFT.

## MS17.P03

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### Crystal engineering of hydroxybenzoic acids. Influence of solvent in the synthon diversity and crystal packing

Seetha Lekshmi Sunil, T.N. Guru Row, *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012 (India)*. E-mail: seetha208@yahoo.co.uk.

Systematic analysis of intermolecular interactions formed between various molecular building units is an interesting topic in the area of crystal engineering. [1] Although the acid-pyridine interactions are well known in literature, the studies pertaining to triazines are relatively rare. Melamine is an interesting candidate due to its symmetry and the availability of several hydrogen bond donor and acceptor functionalities. Further, it is an important compound from the industrial and economical perspective. The recognition patterns of melamine with a series of substituted hydroxybenzoic acids have been studied with the assumption that the OH and COOH groups can make a cooperative influence in the recognition process and results in diverse synthons and supramolecular architectures. All these complexes form solvated assemblies and the solvent of crystallization plays an important role in the structure stability. The molecular adducts exhibit a salt-cocrystal continuum and the formation of the salts cannot be predicted on the basis of  $\Delta pK_a$  values, as most of the molecular candidates have similar  $pK_a$  values.[2] The synthon diversity and the crystal packing in terms of intermolecular interactions provide useful inputs for crystal design.

[1] G.R. Desiraju, *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, **1989**. [2] V.R. Hathwar, R. Pal, T.N. Guru Row, *Crystal Growth & Design*. **2010**, *10*.

**Keywords:** crystal engineering, supramolecular synthon, salt-cocrystal continuum

## MS17.P04

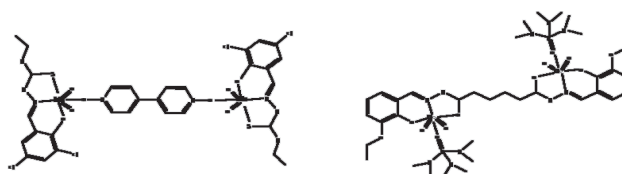
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### Synthesis and structures of binuclear dioxomolybdenum schiff base complexes

Kong Mun Lo, Richard Wong Chee Seng, Ngui Khiong Ngan, *Department of Chemistry, Faculty of Science, University of Malaya, Kuala Lumpur, Malaysia*. E-mail: kmlo@um.edu.my

Two types of binuclear dioxomolybdenum Schiff base complexes were synthesized and their X-ray crystal structures were determined. In the first instant, the reaction of bis(acetylacetonato)dioxomolybdenum with 3,4-dichlorosalicylaldehyde 4-ethylthiosemicarbazide in the presence of 4,4'-bipyridine or 4,4'-bipyridine *N*-oxide gave a binuclear *cis*-dioxomolybdenum complex in which the bidentate ligand, 4,4'-bipyridine or 4,4'-bipyridine *N*-oxide formed a bridge between the two

molybdenum atoms. The overall geometry at each molybdenum site can be regarded as a distorted octahedron, with the equatorial plane formed by the imino nitrogen, phenoxyl oxygen, hydroxyl oxygen of the Schiff base and one of the terminal oxygen atoms of the dioxomolybdenum cation. The other terminal oxygen and the donor atom from the 4,4'-bipyridine or 4,4'-bipyridine *N*-oxide ligand occupy the apical position. In the case of the binuclear dioxomolybdenum complex containing the 4,4'-bipyridine *N*-oxide ligand, the molecules are linked by N-H $\cdots$ O hydrogen bonds into a polymeric chain.



The second type of binuclear dioxomolybdenum(VI) Schiff base complexes was formed by the reaction of bis(acetylacetonato)dioxomolybdenum with 1,4-bis(3-ethoxy-salicylaldehyde carbohydrazonato)butane in the presence of ethanol or hexamethylphosphoramide. In this case, the two molybdenum atoms are not bridged directly by a bidentate ligand, but coordinated at each end to the O,N,O donor atoms of the symmetrical hexadentate Schiff base ligand. Each of the molybdenum atoms also adopts the distorted octahedral configuration with the equatorial plane formed by the imino nitrogen, phenoxyl oxygen, hydroxyl oxygen of the Schiff base and one of the terminal oxygen atoms of the dioxomolybdenum cation. The other terminal oxygen and the donor atom from either ethanol or hexamethylphosphoramide molecule occupy the apical position. In the case of the complex containing the ethanol molecule, adjacent molecules are linked by O-H $\cdots$ N hydrogen bonds into a polymeric chain that runs along the *a*-axis of the monoclinic unit cell.

**Keywords:** Schiff base, dioxomolybdenum

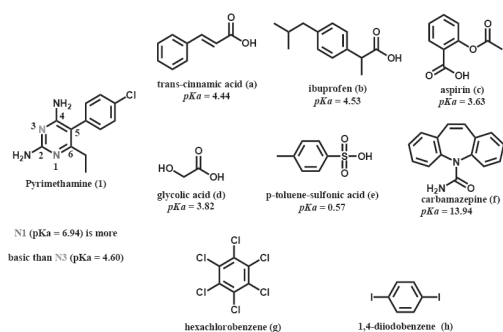
## MS17.P05

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### Is molecular adduct formation predictable?

Amit Delori, William Jones, *Pfizer Institute for Pharmaceutical Materials Science, Department of Chemistry, University of Cambridge, (United Kingdom) CB2 1EW*. E-mail: amitdelori@gmail.com

The purpose of our study was to check the predictability of the formation of molecular adducts using the recently developed hydrogen bond propensity method<sup>1,2</sup>. Six new drug forms **1a-1f** of the anti-malarial drug pyrimethamine, **1** were synthesized with trans-cinnamic acid, **a**; ibuprofen, **b**; aspirin, **c**; glycolic acid, **d**; 4-methylbenzenesulfonic acid, **e** and carbamazepine, **f** respectively. Their crystal structures will be described. Salt formation (by the transfer of the proton from the cofomer to the most basic heteroaromatic nitrogen of pyrimethamine) was observed in all the complexes except **1f**. The attempted cocrystallization reactions (**1g-1h**), of pyrimethamine, with hexachlorobenzene; **g**, and 1,4-diiodobenzene; **h**, respectively were unsuccessful in yielding adducts. Hydrogen bond propensity calculations [1], [2] were carried out to check the predictability of formation/non-formation of these molecular adducts. For **1a-1f**, the bonds of highest propensity were calculated between **1** and the corresponding cofomers rather than self-association, predicting the formation of adducts. In contrast the bonds of highest propensity were calculated for self-association of molecules of **1**, for **1g-1h**, in agreement with the unsuccessful reactions.



**Keywords:** pharmaceutical co-crystallization, hydrogen-bond propensity calculations, supramolecular chemistry

[1] Propensity calculations were carried out by a newer version of mercury software which is under development by CCDC. [2] P.T.A. Galek, L. Fabian, W.D.S. Motherwell, F.H. Allen, N. Feeder, *Acta Crystallogr., Sect. B* **2007**, B63, 768.

### MS17.P06

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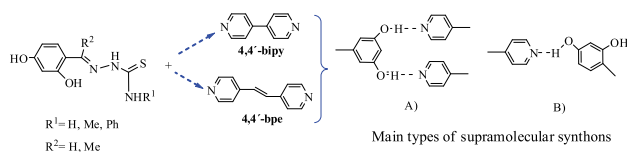
**O-H...N Heterosynthons in co-crystals. Assemblies based on resorcinol derivatives**

Ara Núñez-Montenegro, Rosa Carballo, Ezequiel M. Vázquez-López. *Inorganic Chemistry Department, University of Vigo, Vigo-Galicia (Spain)*. E-mail: aranu@uvigo.es

Multicomponent molecular crystals usually referred to as co-crystals, have recently become into a focus since their potential applications in e.g. synthetic chemistry and pharmaceutical industry. The fact that a co-crystal is obtained reflects that is possible to analyse a few significant intermolecular interactions between chemically distinct components. Such idea leads directly to the concept of heterosynthons, which can describe as hydrogen bonded recognition unit between dissimilar molecules [1].

We have selected a series of pyridines (4,4'-bipyridine and trans-1,2-bis-(4-pyridyl)ethylene) with different derivatives of resorcinol (2,4-dihydroxybenzaldehyde and 2,4-dihydroxyacetophenone thiosemicarbazone) to explore the robustness of hydroxyl-pyridyl heterosynthons. Clearly, by choosing appropriate resorcinols as templates, a rational design of crystals can be achieved. We have used the graphics sets introduced by Etter for motifs generated from intermolecular hydrogen bonds in order to define a hydrogen-bond pattern [2].

The organizational consequences of hydrogen-bonds in the hydroxyl-pyridine heterosynthons in the presence of competitive hydrogen-bonding functional groups were elucidated. Co-crystallization produces discrete structures due to intermolecular hydrogen bonds between O-H...N orienting the pyridine molecules parallel to each other, and the pyridil rings are further stabilized by  $\pi$ - $\pi$  interactions at a distance around 4Å. The ability of resorcinols derivatives to assemble pyridines yields also infinite 1D arrays. The stoichiometric of these co-crystals and the presence of any solvent in the crystallographic net are responsible for the polymorphs found.



[1] A. Mukherjee, G.R. Desiraju, *Chem. Commun.* **2011**, 47, 4090-4092. [2] M.C. Etter, *Acc.Chem.Res* **1990**, 23, 120-126.

**Keywords:** assembly, H-bridge, ayridine, lower cases

### MS17.P07

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**Two in one: A fréchet-type dendron manifesting conformational duality**

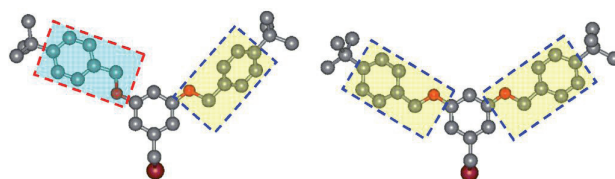
Lydia Brelot,<sup>a</sup> Adrian-Mihail Stadler,<sup>bc</sup> Corinne Bailly,<sup>a</sup> <sup>a</sup>*Service de Radiocristallographie, Institut de Chimie de Strasbourg, France.* <sup>b</sup>*Institut de Science et d'Ingénierie Supramoléculaires, Université de Strasbourg, France.* <sup>c</sup>*Karlsruhe Institute of Technology (KIT), Forschungszentrum Karlsruhe (FZK), Institute for Nanotechnology (INT), (Germany)*. E-mail: brelot@unistra.fr

The molecular structure of a Fréchet-type dendron revealed two different conformers present in the same crystal. This case of conformational duality is described and a detailed analysis is carried out to understand this phenomenon.

The difference of conformation lies in the *m*-di(methyleneoxy)benzene motifs of the dendron, which are oriented in a different way. The low energy difference between the two types of conformation is discussed.

The solid state intermolecular interactions and the crystal packing are also investigated in order to rationalize this conformational duality. Indeed, the structure shows the presence of CH- $\pi$  interactions between the molecules and generates a layered stacking with more or less coplanar molecules.

A comparative analysis is also done on other reported Fréchet-type dendritic structures existing in the Cambridge Structural Database (CSD) and showing conformational duality or diversity. This analysis shows that dendrimers and dendrons based on the *m*-di(methyleneoxy)benzene motif are flexible and this flexibility generates the formation of different conformers despite the existence of some preferred conformations [1].



[1] A.-M. Stadler, L. Brelot, *Crystal Growth & Design* **2010**, 10, 2285-2290.

**Keywords:** conformers, crystal engineering, dendrimer

### MS17.P08

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**Inclusion compounds as secondary building units for supramolecular chemistry**

José A. Fernandes, Ana I. Ramos, Paulo J. A. Ribeiro-Claro, Susana S. Braga, Filipe A. Almeida Paz, *CICECO, Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-193 Aveiro (Portugal)* E-mail: jafernandes@ua.pt

In last few years the field of coordination chemistry has seen a great rebirth due to the intense research concerning the synthesis, isolation and structural characterisation of Metal-Organic Frameworks (MOFs).